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Difference in photoirradiation effects between poly(*p*-phenylene vinylene) derivative and poly(3-alkylthiophene) as electroluminescent materials*

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1. Introduction

Conducting polymers in undoped state show semiconducting properties and some of them can be used as electroluminescent materials.[1-3] Some of the conducting polymers are soluble to common organic solvent, and solution-based processing such as spin-coating or printing techniques gives high-quality large-area polymer films suitable for electronic devices including light-emitting devices, photovoltaic devices, and field-effect transistors. However, the conducting polymers are known as photosensitive materials, that is, they degrade upon photoirradiation in air. From an elemental consideration, it is expected that the photo-degradation mechanism of conducting polymers may consist of, at least, two elemental phenomena: the scission of main chain and the introduction of defects including oxygen.[4]

If we think about the photo-degradation effects on polymer light-emitting devices based on conducting polymers, it is expected that the above-mentioned two elemental phenomena should affect the device performance in different ways. Thus, for understanding the photo-degradation mechanism of polymer light-emitting devices, studying with the real devices is crucially important. Recently, we have proposed to study the photo-degradation of polymer light-emitting devices by using devices with a semitransparent cathode. When the thickness of the cathode is sufficiently thin, the photo-degradation rate of the polymer film in the devices is almost the same to the naked film, allowing us to direct comparison of changes in the device characteristics with those in the properties of naked polymer film.

In this paper, we report the photo-degradation phenomena in poly(2-methoxy-5-dodecyloxy-*p*-phenylene vinylene) (MDOPPV) and poly(3-dodecylthiophene) (PAT12), and discuss about the difference between them.

2. Experimental

Figure 1 shows the device structure used in this study as well as the molecular structures of the polymers. The thickness of the polymer films was on the order of 100 nm. The optical transmittance of the Al films coated on glass pieces was used as an index of the cathode thickness. From our previous

*In honor of Professor Katsumi Yoshino of Osaka University on the occasion of his *Kanreki* (60th birthday).

studies, it is confirmed that the photo-degradation rate of the polymer film in the device is almost identical to the naked polymer film when the transmittance of Al cathode was about 30%. The emission area of the devices was $1 \times 1 \text{ cm}^2$. The photoirradiation to the devices was carried in the slide chamber of a slide projector with 150W incandescent lamp. Another polymer films coated on glass plates were used for optical measurement (UV-VIS absorption and photoluminescence spectra).

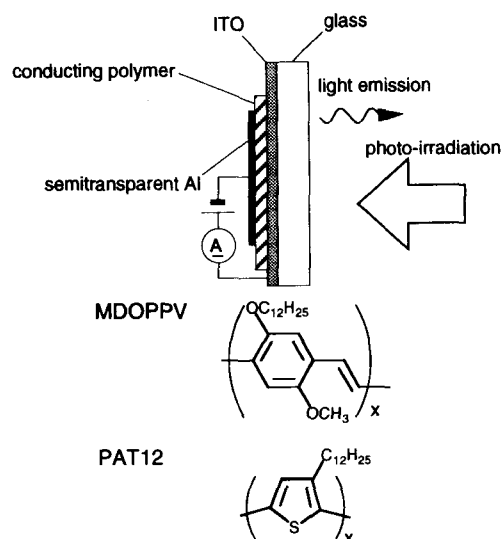


Fig. 1 Schematic structure of the polymer light-emitting devices and molecular structures of polymers used in this study.

3. Results and discussion

Figure 2(a) shows the emission intensity-voltage characteristics of polymer light-emitting devices based on MDOPPV at various photo-irradiation periods. The emission intensity at a constant voltage rapidly dropped upon photoirradiation to be undetectably weak within several minutes.

As previously noted, photo-degradation mechanism of conducting polymers may consist of, at least, two elemental phenomena, that is, the scission of main chain and the introduction of photooxidized defects. The former phenomenon, the scission of main chain, may affect the carrier transport/injection ability of conducting polymer to decrease the supply of parent carriers to form excitons. Thus, the emission intensity of the device will drop.

On the other hand, the latter may reduce the probability of radiative decay of singlet excitons, since it is known that the photooxidized defects in conducting polymers such as carbonyl group in poly(*p*-phenylene vinylene) separate the singlet excitons to the positive and negative carriers to quench the

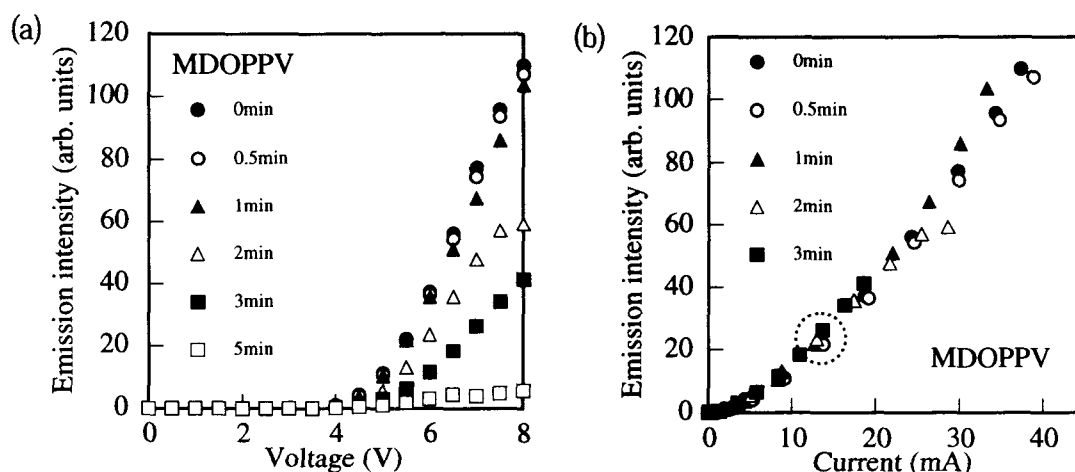


Fig. 2 (a) Emission intensity-voltage and (b) emission intensity-current characteristics of polymer light-emitting device based on MDOPPV at various photoirradiation periods.

luminescence.[4] And thus, the emission intensity of the device will drop. Although the two phenomena will result in apparently the same situation, the difference in the mechanism will be reflected in the quantum efficiency of the device. That is, the scission of main chain may not change the quantum efficiency while the defect quenching may reduce the quantum efficiency effectively.

The emission intensity-current characteristics of the MDOPPV device did not show any notable change as shown in Fig. 2(b), implying that the external quantum efficiency of the device remains constant. Thus, we can conclude that not the defect quenching but the reduced carrier transport ability due to scission of main chain originates the photo-degradation of MDOPPV-based devices.

On the other hand, the photoluminescence from the MDOPPV film excited at 350 nm, where the absorption coefficient of the MDOPPV film does not change upon our photoirradiation condition, drastically weakened due to the same photoirradiation condition. Since the quantum efficiency of the electroluminescence must be proportional with the quantum efficiency of the photoluminescence, our observations seem to be somewhat curious. However, if we take the difference in the origin and the microscopic distribution of excitons in polymer films into account, these observations can be reasonably understood.

In photoluminescence process, the polymer film is uniformly excited and the excitons are formed uniformly throughout the polymer film, regardless of the existence of photooxidized defects. Thus, some excitons are formed near the quenching defects and others are not. The excitons accidentally formed near or migrated to the defects will be readily quenched, to drop the quantum efficiency.

On the other hand, in electroluminescence process, the creation of excitons is a result of the recombination of parent positive and negative charge carriers. Therefore, the electrically generated excitons may be formed only on the carrier transport path. From elemental consideration, it is expected that the carrier transport path is interrupted at the photooxidized defects, and thus, the electrically generated excitons must not be formed near the quenching defects. In other words, the recombination zone is spatially separated from the quenching defects.

Figure 4(a) shows the emission intensity-voltage characteristics of the polymer light-emitting devices based on PAT12. Similar to the case of MDOPPV-based devices, the emission intensity of the PAT12-based devices rapidly dropped. However, as shown in Fig. 4(b), the slope in the emission intensity-current characteristics decreased with prolonged photoirradiation, in contrast to the MDOPPV case. That is, not only the emission intensity but also the external quantum efficiency of the devices reduced

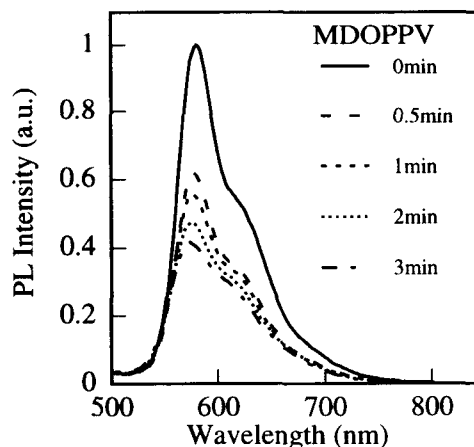


Fig. 3 Photoluminescence spectrum of an MDOPPV film at various photoirradiation periods (excitation wavelength =400 nm).

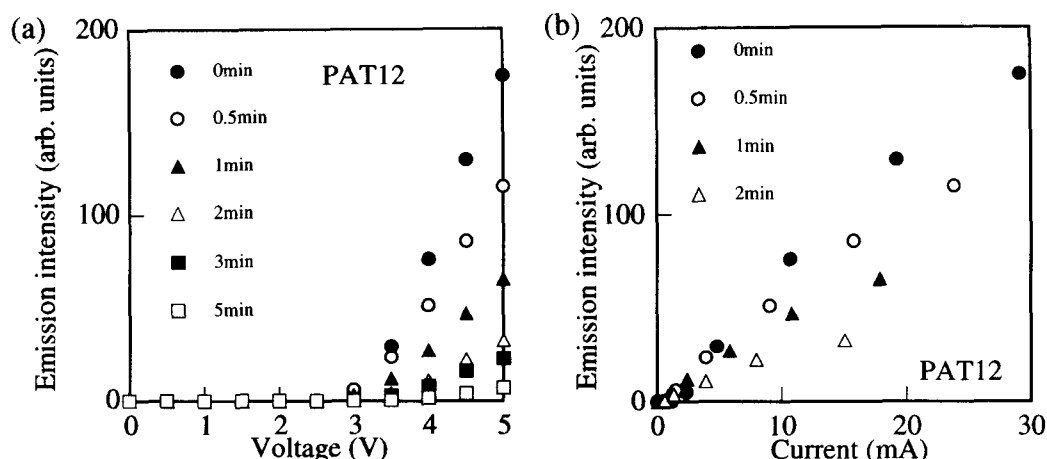


Fig. 4 (a) Emission intensity-voltage and (b) emission intensity-current characteristics of polymer light-emitting device based on PAT12 at various photoirradiation periods.

upon photoirradiation, suggesting that the defect quenching of singlet excitons plays an important role for photo-degradation of PAT12-based devices.

Upon photoirradiation for several minutes, the optical absorption spectrum of PAT12 film did not show any notable change while the electroluminescence was completely quenched, suggesting that quite low concentration of defects effectively quenches the electroluminescence.

The change of photoluminescence spectra of the PAT12 film due to photoirradiation may give critical information about photo-degradation mechanism of PAT12-based device. However, because of the lack of sensitivity of our measurement apparatus, we could not detect any photoluminescence from the PAT12 film.

4. Conclusion

Photoirradiation effects on the luminescent conducting polymers, MDOPPV and PAT12 were studied. It was found that although the emission intensity-voltage characteristics of both polymers change similarly, their emission intensity-current characteristics tell the difference in the degradation mechanism. That is, the external quantum efficiency of PAT12-based devices drastically dropped upon photoirradiation but that of MDOPPV-based devices remained constant, suggesting that the defect quenching of luminescent species plays an important role in the case of PAT12 but not in the MDOPPV case.

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